

Cu₃N Nanocubes for Selective Electrochemical Reduction of CO₂ to Ethylene

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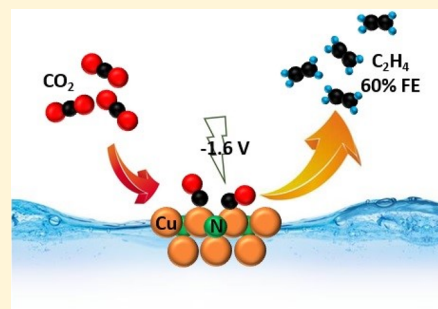
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Supporting Information

ABSTRACT: Understanding the Cu-catalyzed electrochemical CO₂ reduction reaction (CO₂RR) under ambient conditions is both fundamentally interesting and technologically important for selective CO₂RR to hydrocarbons. Current Cu catalysts studied for the CO₂RR can show high activity but tend to yield a mixture of different hydrocarbons, posing a serious challenge on using any of these catalysts for selective CO₂RR. Here, we report a new perovskite-type copper(I) nitride (Cu₃N) nanocube (NC) catalyst for selective CO₂RR. The 25 nm Cu₃N NCs show high CO₂RR selectivity and stability to ethylene (C₂H₄) at −1.6 V (vs reversible hydrogen electrode (RHE)) with the Faradaic efficiency of 60%, mass activity of 34 A/g, and C₂H₄/CH₄ molar ratio of >2000. More detailed electrochemical characterization, X-ray photon spectroscopy, and density functional theory calculations suggest that the high CO₂RR selectivity is likely a result of (100) Cu(I) stabilization by the Cu₃N structure, which favors CO–CHO coupling on the (100) Cu₃N surface, leading to selective formation of C₂H₄. Our study presents a good example of utilizing metal nitrides as highly efficient nanocatalysts for selective CO₂RR to hydrocarbons that will be important for sustainable chemistry/energy applications.

KEYWORDS: CO₂ reduction, copper(I) nitride, perovskite structure, nanocubes, ethylene formation



Active and selective CO₂ reduction reaction (CO₂RR) is an essential step to recycle the overproduced CO₂ back to reusable forms of carbon and to build an energy-sustainable society.^{1–3} Electrochemical CO₂RR can proceed under ambient conditions and has been studied extensively to understand catalysis fundamentals and to develop efficient catalysts for practical applications.^{4–8} Among all nanostructured catalysts tested thus far, nanostructured Cu catalysts are unique to catalyze CO₂RR to hydrocarbons.^{9–14} However, past studies also show that it is difficult to control Cu surface catalysis under ambient conditions, and the reaction often leads to the formation of a mixture of hydrocarbons, which makes the separation of a specific hydrocarbon product extremely challenging. Recently, a flow-cell design was used to convert CO₂ more selectively to hydrocarbons, especially to ethylene (C₂H₄) with the Faradaic efficiency (FE) reaching up to 70%.^{15,16} However, this cell device does require corrosive alkaline electrolyte, such as 10 M KOH, to realize the desired conversion.

Here, we introduce perovskite-structured copper(I) nitride (Cu₃N) nanocubes (NCs) as a new catalyst for selective CO₂RR to ethylene (C₂H₄) under ambient conditions. Nanostructured transition metal nitrides have been studied for electrocatalytic reactions,^{17,18} but a very limited number of

metal nitrides were tested for CO₂RR. Ni₃N was studied for CO₂RR to CO.¹⁹ Cu₃N nanowires prepared from nitridation of Cu(OH)₂ nanowires were converted to multigrained Cu nanowires to show high CO₂RR selectivity to C₂ products²⁰ due likely to the semiconductivity of Cu₃N.²¹ Different from these nitride catalysts, our Cu₃N NCs have a phase-pure anti-ReO₃ perovskite-type structure,²² and in 0.1 M KHCO₃ electrolyte solution, they catalyze the CO₂RR to C₂H₄ with 60% FE and 34 A/g Cu mass activity at −1.6 V vs RHE. More importantly, the NC catalyst suppresses the formation of CH₄ in the gas-phase products with a C₂H₄/CH₄ molar ratio of >2000, the highest selectivity ever reported for Cu-based CO₂RR catalysis. Our Cu₃N NC structure is also stable in the CO₂RR condition, showing only 7% FE decrease (from 60 to 53%) under continuous electrolysis for 20 h. The combined ease of synthesis and high CO₂RR catalytic selectivity and durability make the Cu₃N NCs a promising new catalyst for practical CO₂RR to C₂H₄, an important industry feedstock used to produce ethylene oxide, ethylene dichloride, ethylbenzene, and polyethylene.

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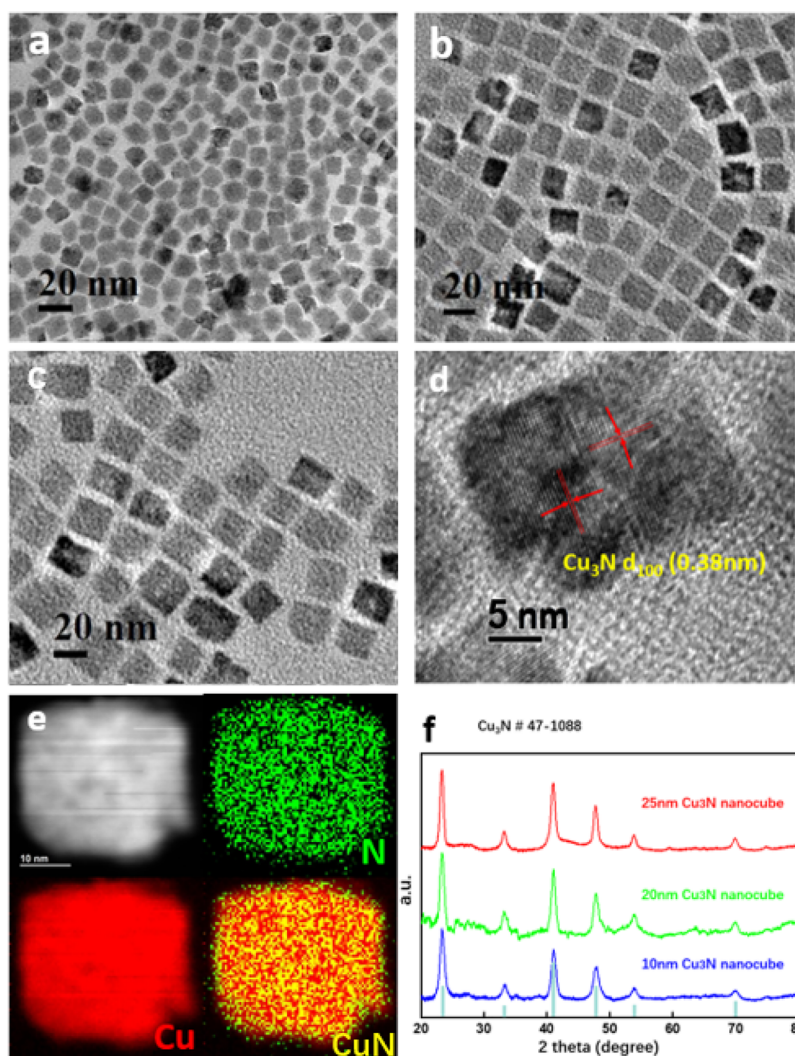


Figure 1. Characterizations of Cu_3N NCs. (a–c) Low-resolution TEM images of the as-synthesized 10 nm (a), 20 nm (b), and 25 nm (c) Cu_3N NCs. (d) High-resolution TEM image of a representative 25 nm Cu_3N NC, showing lattice fringe along the $\langle 100 \rangle$ direction. (e) HAADF-STEM image of Cu_3N NC and the corresponding STEM-EELS elemental mapping of the NC. (f) XRD patterns of the 10, 20, and 25 nm Cu_3N NCs, showing typical diffraction patterns that correspond to the perovskite-type $Pm\bar{3}m$ structure.

Cu_3N NCs were synthesized by modifying a published method.²³ First, 25 nm Cu_3N NCs were prepared by partially reducing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with octadecylamine/oleylamine (2.5g/2.5 mL, $\sim 1/0.8$ mass ratio; see [Supporting Information](#) for details) at 240 °C, whereas 20 and 10 nm NCs were made at 250 and 260 °C, respectively. These synthetic results indicate that higher reaction temperature initiates faster nucleation, consuming more Cu precursor in the nucleation stage and leading to the formation of smaller NCs. Another observation is that the formation of cubic Cu_3N requires the reaction temperature to be at 240 °C or above. Low reaction temperatures took longer times for the Cu precursor to nucleate, and the Cu_3N seeds obtained from this slow nucleation event may be defected. It is difficult for the defected seeds to grow into NCs.²⁴ As a result, at 230 °C, 20 nm sphere-like Cu_3N nanoparticles (NPs) were separated. [Figure 1a–c](#) shows transmission electron microscopy (TEM) images of the as-synthesized Cu_3N NCs with lateral dimensions at 9.7 ± 0.4 , 20.0 ± 0.7 , and 25.0 ± 1.5 nm, and [Figure S1](#) shows the TEM image of the 20 nm Cu_3N NPs. High-resolution TEM (HRTEM) of a representative 25 nm

Cu_3N NC ([Figure 1d](#)) shows clear lattice fringes with their interfringe distance at 0.38 nm, which is close to interplanar distance of the $\langle 100 \rangle$ planes of the cubic Cu_3N $Pm\bar{3}m$ structure. High-angle annular dark-field scanning TEM (HAADF-STEM) and STEM electron energy loss spectroscopy (STEM-EELS) ([Figure 1e](#)) show that the Cu and N are uniformly distributed across the cubic structure. X-ray diffraction (XRD) patterns of the 10, 20, and 25 nm Cu_3N NC powders further confirms that the NCs have the cubic $Pm\bar{3}m$ structure ([Figure 1f](#)), which is an anti- ReO_3 perovskite structure.²² These Cu_3N NCs are colloidal and chemically stable under ambient conditions as they showed neither aggregation nor obvious sign of surface oxidation 2 weeks after their hexane dispersion was exposed to air ([Figure S2](#)). Annealed at 200 °C under Ar for 2 h, the Cu_3N NCs showed no structure change ([Figure S3](#)), but at 300 °C for 2 h, they were converted to Cu NPs ([Figure S4](#)), which was further confirmed by thermal gravimetric analysis (TGA) ([Figure S5](#)). As these Cu_3N NCs are stable under ambient conditions, they are a viable catalyst for studying CO_2RR .

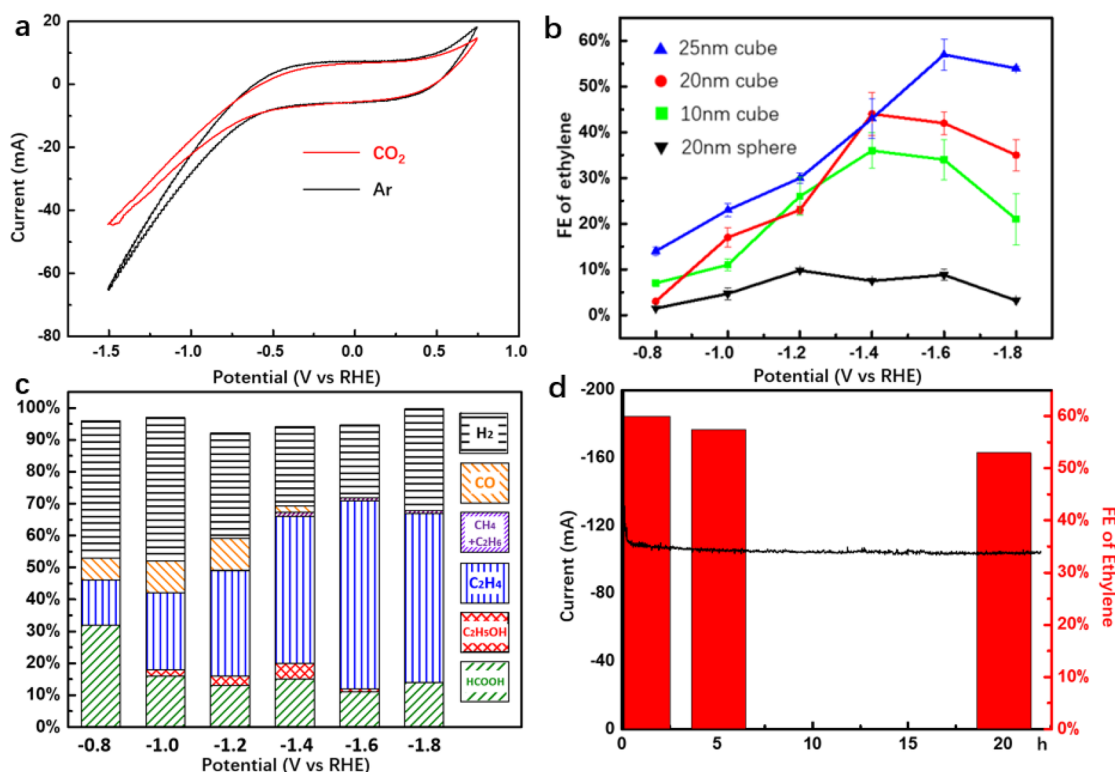


Figure 2. Cu₃N-catalyzed CO₂RR in 0.1 M KHCO₃ solution. (a) CV curves of Cu₃N NCs under Ar (black) and CO₂ (red) atmosphere. (b) Potential-dependent ethylene formation FE of CO₂RR catalyzed by different Cu₃N catalysts. (c) Products distribution of CO₂RR catalyzed by 25 nm Cu₃N NC catalyst at different reduction potentials. (d) Reduction current change (black) and ethylene formation FE (red) over time during the continuous CO₂RR catalyzed by 25 nm NCs at -1.6 V.

The Cu₃N NCs were deposited on Ketjen carbon (Figure S6) and painted on carbon paper (Toray TGP-H-060) for electrochemistry and electrocatalytic CO₂RR studies in 0.1 M KHCO₃ (see Supporting Information for details). The cyclic voltammetry (CV) curve of the 25 nm Cu₃N NCs under an Ar atmosphere shows no Cu redox peaks (Figure 2a), which is different from what is commonly observed from the Cu NP catalyst,²⁵ indicating that there is no measurable metallic Cu on the Cu₃N NC surface. Other Cu₃N NCs and Cu₃N NPs show similar CV behaviors (Figure S7). The increased current after -0.5 V is attributed to proton reduction (hydrogen evolution reaction (HER)). CV under CO₂ atmosphere is similar to that under Ar condition except the decrease of the current after -0.5 V (Figure 2a) due to the competition between CO₂RR and HER.²⁶

With continuous CO₂ flow, electrochemical CO₂RR was tested under different potentials, and the gas/liquid products were characterized by gas chromatography and ¹H NMR (see Supporting Information for details). The potential-dependent FEs of C₂H₄ formed in the presence of different Cu₃N catalysts are listed in Figure 2b. The general trend is that the larger the NCs, the better the CO₂RR selectivity. Other smaller NCs are less effective, and their peak FEs reach 45% (20 nm NCs) and 35% (10 nm NCs) at -1.4 V. The spherical 20 nm Cu₃N NP catalyst is least active with the FE of C₂H₄ being less than 10% in the reduction potential range tested. The 25 nm Cu₃N-catalyzed CO₂RR generates C₂H₄ (14% FE) at -0.8 V. At -1.6 V, the FE of C₂H₄ reaches the maximum 60% with the mass activity of 34 A/g and current density of 30 mA/cm² (Figure S8), and their overall CO₂RR results are summarized in Figure 2c. In addition to C₂H₄, the gas products obtained

from various reduction potentials also contain H₂ (<40% FE) from HER and CO (<9% FE) (CO was undetectable at -1.6 V or beyond). The liquid-phase products separated from the reaction contain only formate (<33% FE) and ethanol (<5.7% FE) over the potential range we studied. The 25 nm Cu₃N-catalyzed CO₂RR is most selective at -1.6 V for generating C₂H₄ (60%) with remarkable current density (the ¹H NMR spectrum of the corresponding minor liquid products HCOOH and ethanol is shown in Figure S9). We measured the capacitive behaviors of the Cu₃N NCs in a potential range from -0.05 to 0.05 V at different scanning rates and obtained their double-layer capacitance of 4.34 mF/cm² (Figure S10), which is 150 times larger than the standard capacitance of the smooth Cu electrode (0.029 mF),²⁷ suggesting that high current density observed from the CO₂RR originates from the large electrochemical surface area of the NC electrode.

We should note that, compared with the common Cu metal catalyst, our Cu₃N catalyst shows higher CO₂RR overpotentials due most likely to the decrease in electron conductivity of the Cu₃N structure. However, because 25 nm Cu₃N NCs are more active and selective than smaller Cu₃N NCs or Cu₃N NPs for the CO₂RR to C₂H₄, it is evident that Cu₃N NCs with larger fractions of (100) facets are especially selective to catalyze CO₂RR to C₂H₄. Another important feature of the Cu₃N NC catalysis is that the catalyst suppresses the formation of C₂H₆ and CH₄ (only <1% FE of C₂H₆ + CH₄ was detected) and shows the highest C₂H₄/CH₄ ratio (>2000) ever reported for the Cu-catalyzed CO₂RR.²⁸

The stability of the Cu₃N-catalyzed CO₂RR was studied at -1.6 V (Figure 2d). The reduction current decreased from 135 mA in the first hour to 101 mA 20 h after the continued

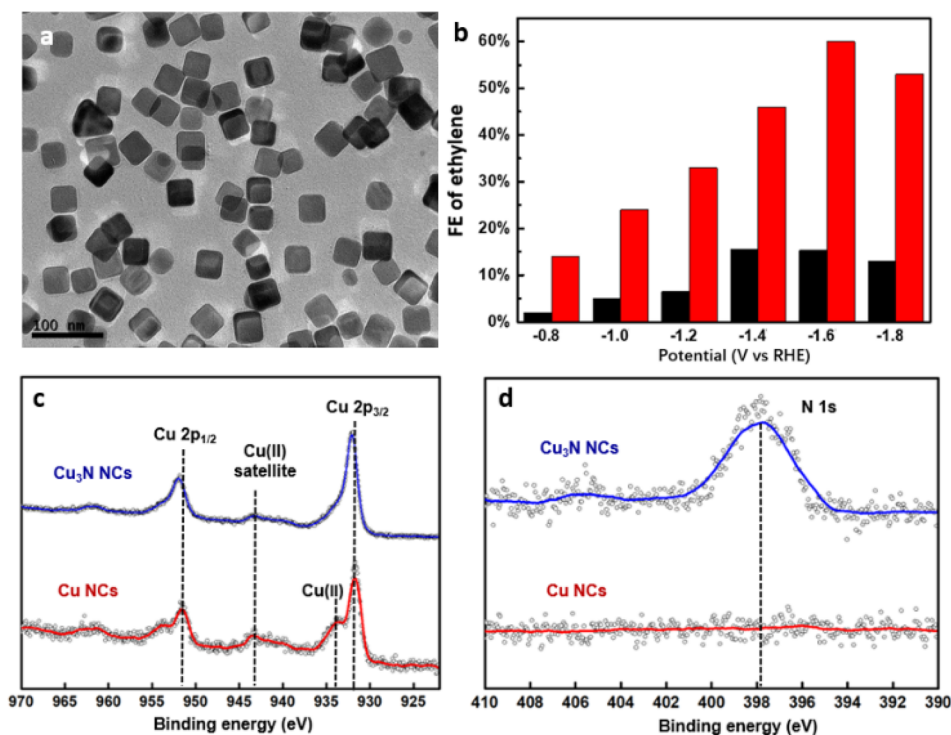


Figure 3. Catalytic performance and surface properties of Cu and Cu₃N catalysts. (a) TEM image of as-synthesized 29 nm Cu NCs. (b) Reduction-potential-dependent FE of ethylene obtained from CO₂RR catalyzed by 25 nm Cu₃N NCs (red) and 29 nm Cu NCs (black). (c) XPS of Cu and Cu₃N NCs showing Cu 2p and Cu(II) peaks. Cu/Cu(I) peaks are too close to separate from the spectra. (d) XPS of Cu and Cu₃N NCs showing N 1s binding energy.

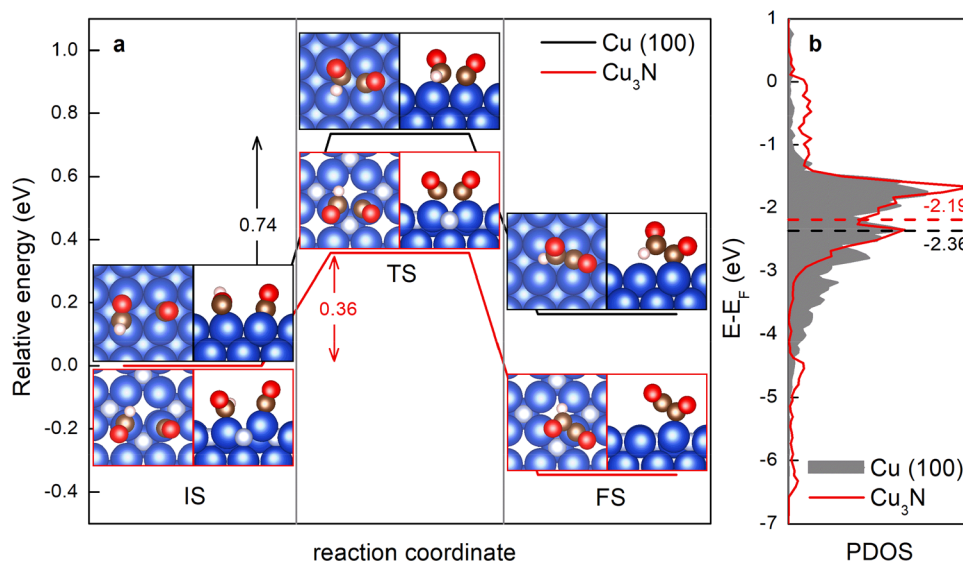


Figure 4. Relative free energy diagram and electronic density of states. (a) Relative free energy diagram for the coupling between CHO_{ads} and CO_{ads} on the Cu(100) and Cu₃N(100) surfaces, respectively. The optimized atomic geometries of the initial, transition, and final states are shown in the insets. Blue, blue gray, gray, red, and white spheres represent Cu, N, C, O, and H atoms, respectively. (b) Calculated density of states of the d-band on the Cu(100) and Cu₃N(100) surfaces. The horizontal dashed lines indicate the d-band centers.

electrolysis. The C₂H₄ formation FE was at 60% in the first hour and was stabilized at around 53%. The TEM image of the Cu₃N NCs after the 20 h of electrolysis (Figure S11) shows that there is only a small degree of NC aggregation, which supports why there is the 7% FE decrease from 60 to 53% during the 20 h electrolysis at -1.6 V. Compared to Cu-based nanocatalysts, especially Cu NCs,^{29–31} reported previously with very limited stability in the selected CO₂RR condition,

our Cu₃N NCs show much enhanced stability, suggesting that N³⁻ stabilizes Cu⁺ more efficiently in the perovskite-type Cu₃N structure.

To confirm that the high CO₂RR selectivity to C₂H₄ is from the Cu₃N(100) and not from Cu(100), we prepared 29.3 ± 3.2 nm Cu NCs, denoted as 29 nm Cu NCs (Figure 3a),³² and studied/compared their electrochemical CO₂RR with 25 nm Cu₃N NCs. As seen in Figure 3b, on Cu NCs, C₂H₄ is

produced starting from -0.8 V, and the highest FE of C_2H_4 is about 15.4% at -1.4 V. As a comparison, the Cu_3N NCs show much higher CO_2RR selectivity to C_2H_4 in all reduction potentials from -0.8 to -1.8 V. As both 29 nm Cu NCs and 25 nm Cu_3N NCs have similar sizes and cube morphology, the superior CO_2RR performance of Cu_3N NCs over Cu NCs suggests that the Cu–N units in the Cu_3N NC structure is essential for the NCs to achieve high CO_2RR selectivity toward C_2H_4 .

To identify which Cu oxidation state, Cu(0) or Cu(I), on the Cu_3N surface dominates the CO_2RR selectivity, we studied surface Cu oxidation and reduction properties of both Cu and Cu_3N NCs using X-ray photoelectron spectroscopy (XPS) and CV. The XPS of Cu NCs shows typical Cu 2p peaks at 932 and 952 eV, as well as two Cu(II) peaks at 934 and 944 eV (Figure 3c), but they are free from N 1s peak (Figure 3d), indicating that the Cu NC surface has Cu, Cu(I), and Cu(II) components. Cu_3N NCs also show two Cu 2p peaks that slightly shift to higher energies and a nearly invisible Cu(II) peak. This indicates that, unlike Cu NCs, the Cu_3N NCs have Cu(I) enriched on their surfaces. The N 1s peak is around 398 eV (Figure 3d), close to the common value (~ 397 eV) observed from metal nitrides. CV of the Cu NCs in Ar-saturated 0.1 M $KHCO_3$ solution exhibit two reduction peaks at 0.35 V (Cu(II)/(Cu(I))) and -0.05 V (Cu(I)/Cu) (Figure S12), indicating that the Cu NC surface after the oxidation scan is surrounded with Cu(II) and Cu(I). These two reduction peaks shift to more positive potentials under CO_2 -saturated conditions due likely to the CO_2 interaction with Cu(I)/Cu(II). Under the same CV scanning condition, Cu_3N NCs show no obvious reduction peaks (Figure 2a), indicating that, on the Cu_3N surface, Cu^+ is better stabilized by N^{3-} , and Cu–N must show the desired synergistic effect on selective CO_2RR to C_2H_4 .

We performed density functional theory (DFT) calculations to elucidate why Cu_3N NCs are so selective for the CO_2RR to C_2H_4 . As C–C coupling is essential for the formation of C_2 products, such as C_2H_4 , we focus on the relevant C–C coupling reactions on the $Cu_3N(100)$ surface. Previous work³³ has established that the C–C bond can be formed on a Cu(100) surface via the coupling between two CO^* molecules (to form $OCCHO_{ads}$) or between CHO^* and CO^* (to form $OCCHO_{ads}$). Our calculations show that the CO–CO coupling is not favored on the $Cu_3N(100)$ surface, whereas the CO–CHO coupling has the energy benefits, as shown in Figure 4a. The free energy barrier for the formation of $OCCHO_{ads}$ on the $Cu_3N(100)$ surface is 0.36 eV, less than half of that on the Cu(100) surface (0.74 eV). From the atomic structures of the initial, transition, and final states of the CHO–CO coupling reaction (inset of Figure 4a), we can see that, on the Cu(100) surface, CHO_{ads} , CO_{ads} , and $OCCHO_{ads}$ occupy the Cu bridge sites, whereas on the $Cu_3N(100)$ surface, they are stabilized on the Cu(I) top sites due likely to the upshift of the Cu d-band center on the Cu_3N surface relative to the Cu(100) surface (Figure 4b), as well as the N^{3-} -induced protonation of CO to CHO. The high energy barrier for the CO–CO coupling on the Cu_3N surface suggests that the CO–CO pathway leading to the formation of C_2 products is suppressed, leaving the CO–CHO coupling a dominant pathway to C_2H_4 .^{34–36}

In this work, we report a new catalyst based on Cu_3N NCs for electrochemical CO_2RR . Among 10, 20, and 25 nm NCs studied, the 25 nm Cu_3N NCs show the highest activity and

selectivity to convert CO_2 to C_2H_4 with FE reaching 60%. More importantly, at the C_2H_4 formation potential (-1.6 V), C_2H_4 is the dominant gas product with the C_2H_4/CH_4 ratio being >2000 , and liquid products contain mostly formate ($<15\%$ FE), which makes the separation of C_2H_4 from the CO_2RR practical. Our studies confirm that Cu(I) is stabilized by N in the Cu_3N structure, and the stabilized Cu(I) is key for the (100) Cu(I) to show enhanced CO_2RR selectivity to C_2H_4 . DFT calculations suggest that the stabilized (100) Cu(I) sites are energetically favored for CO–CHO (not CO–CO) coupling, inferring that the formation of $COCHO_{ads}$ is a dominant pathway in the Cu_3N -catalyzed CO_2RR to C_2H_4 . This Cu_3N -induced catalysis enhancement on selective CO_2RR may offer a new direction to develop highly efficient nanocatalysts for selective CO_2RR to C_2H_4 or other hydrocarbons.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b03324.

Experimental procedures and supporting Figures S1–S12 (PDF)

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Notes

The authors declare no competing financial interest.

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